

INFRARED SPECTRA OF LIEBIGITE, ANDERSONITE, VOGLITE, AND SCHROECKINGERITE*,**

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Received November 7th, 1977

Infrared spectra of mineral possessing layer structure — liebigite, $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot (8-11) \text{H}_2\text{O}$, schroeckingerite, $\text{NaCa}_3[\text{UO}_2(\text{CO}_3)_3]\text{SO}_4\text{F} \cdot 10 \text{H}_2\text{O}$, voglite, $\text{Ca}_2\text{Cu}[\text{UO}_2(\text{CO}_3)_4] \cdot 6 \text{H}_2\text{O}$ (?), and synthetic andersonite, $\text{Na}_2\text{Ca}[\text{UO}_2(\text{CO}_3)_3] \cdot 6 \text{H}_2\text{O}$ — were measured and interpreted and compared with the published infrared spectra of ammonium, potassium, rubidium, and cesium dioxo-tricarbonatouranates(VI). From the analysis of the infrared spectra it follows — in accordance with the results of X-ray diffraction analysis — that in the dioxo-tricarbonatouranate(VI) complex anion, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, forming hexagonal bipyramid, three bidentately bonded carbonate groups are present in the equatorial plane (in liebigite and andersonite and apparently also in schroeckingerite and voglite). The coordinations of the SO_4^{2-} and F^- ions in schroeckingerite and of the fourth carbonate group (?) in voglite have not been elucidated.

Liebigite, andersonite, schroeckingerite, and voglite are uranium secondary minerals, generally classed with layer or insular uranium carbonates. While liebigite, $\text{Ca}_2 \cdot [\text{UO}_2(\text{CO}_3)_3] \cdot (8-11) \text{H}_2\text{O}$, and andersonite, $\text{Na}_2\text{Ca}[\text{UO}_2(\text{CO}_3)_3] \cdot 6 \text{H}_2\text{O}$, have been described in detail, prepared artificially, and examined as to their structures¹, for schroeckingerite, $\text{NaCa}_3[\text{UO}_2(\text{CO}_3)_3] \text{SO}_4\text{F} \cdot 10 \text{H}_2\text{O}$, the synthesis has been described, the lattice parameters have been determined and three possible corresponding point symmetry groups established. The location of the atoms in the crystal lattice is not so far known (for a detailed treatment of schroeckingerite see²). Very little is known about voglite, which has not yet been synthesized. It is usually characterized by the formula³ $\text{Ca}_2\text{Cu}[\text{UO}_2(\text{CO}_3)_4] \cdot 6 \text{H}_2\text{O}$, apparently based on the only analysis known, performed as long as 120 years ago. The small quantities of this mineral available do not thus far permit a new chemical analysis and determination of the chemical composition. In the paper⁴ we have dealt with the data on voglite available and confronted them with the results of our study of voglite samples from the mineralogical collection of the National Museum in Prague. We have also presented the X-ray diffraction patterns of these voglite samples.

* Part IV in the series Chemistry of Uranyl Carbonates; Part III: This Journal 44, 1 (1979).

** Presented in condensed form at the XI. National Conference on Inorganic Chemistry Pardubice, September 6–8th, 1977.

In this work, the IR spectra of liebigit and voglite are described and elucidated for the first time (except for the notes^{1,2,4}). The IR spectra of schroeckingerite and andersonite have been described by Huang and Kerr⁵; their results are here compared with our data.

This work is part of systematic revision of minerals from the collection of the National Museum in Prague.

EXPERIMENTAL

The minerals studied are listed in Table I. Two minerals denoted as voglite in the collection of the National Museum in Prague are in fact metatorbernite⁴, as follows from the X-ray dif-

TABLE I

Characterization of the Minerals Studied

All the minerals belong to the collection of the National Museum in Prague.

Deposit	Designation (inv. no)
Liebigit, $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot (8-11) \text{H}_2\text{O}$	
Schneeberg, GDR	M 25 — NM 15 691
Jáchymov, Czechoslovakia	M 27 — NM 25 017
Jáchymov, Czechoslovakia	M 31 — NM 48 847
Jáchymov, Czechoslovakia	M 32 — NM 71 624
Jáchymov, Czechoslovakia	M 38 — NM 15 695
Johanngeorgenstadt, GDR	M 43 — NM 15 698
Jáchymov, Czechoslovakia	M 45 — NM 36 542
Jáchymov, Czechoslovakia	M 47 — NM 39 060
Schroeckingerite, $\text{NaCa}_3[\text{UO}_2(\text{CO}_3)_3]\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	
Jáchymov, Czechoslovakia	M 50 — NM 4 881
Jáchymov, Czechoslovakia	M 51 — NM 4 882
Jáchymov, Czechoslovakia	M 52 — NM 15 701
Jáchymov, Czechoslovakia	M 53 — NM 15 702
Jáchymov, Czechoslovakia	M 54 — NM 15 703
Red Desert, Wamsutter, Wyoming, USA (dakeite)	M 65 — NM 48 975
Voglite, $\text{Ca}_2\text{Cu}[\text{UO}_2(\text{CO}_3)_4] \cdot 6 \text{H}_2\text{O} (?)$	
Jáchymov, Czechoslovakia	M 17 — NM 15 699
Jáchymov, Czechoslovakia	M 18 — NM 15 700
Jáchymov, Czechoslovakia	M 19 — NM 45 172
Jáchymov, Czechoslovakia	M 20 — NM 45 181

fraction analysis, and therefore are not reported. Synthetic andersonite, $\text{Na}_2\text{Ca}[\text{UO}_2(\text{CO}_3)_3] \cdot 6\text{H}_2\text{O}$, was prepared according to the method⁶.

The IR spectra of the minerals were measured on a spectrophotometer Perkin-Elmer 225 in KBr microdisks by employing a beam condenser. The various minerals were identified by X-ray diffraction analysis using the Debye-Scherrer powder method on an apparatus Mikrometa, Chirana (CuK_α radiation, Ni filter, chamber 114.6 mm, exposition 6 h, 20 mA, 40 kV), and in some instances also by measuring the refractive indices. Liebigit, schroekingierite, and synthetic andersonite were investigated also by thermal analysis.

RESULTS AND DISCUSSION

The linear uranyl group, UO_2^{2+} , has four normal vibrations⁷⁻¹⁰ but three fundamental bands only:

- ν_1 ($900-700\text{ cm}^{-1}$) – symmetric stretching fundamental, only Raman-active;
- ν_2 ($260-180\text{ cm}^{-1}$) – doubly degenerate bending fundamental, only IR-active;
- ν_3 ($1000-850\text{ cm}^{-1}$) – antisymmetric stretching fundamental, only IR active.

Distorsion of the uranyl group or change in the local symmetry can result in the removal of degeneracy of the ν_2 mode and IR activation of the ν_1 mode.

Vibrations of a free CO_3^{2-} group give rise to four fundamentals: ν_1 ($1115-1050\text{ cm}^{-1}$) – symmetric stretching vibration, ν_2 ($880-835\text{ cm}^{-1}$) – out-of-plane bending vibration, ν_3 ($1610-1250\text{ cm}^{-1}$) – doubly degenerate stretching vibration, ν_4 (770 to 670 cm^{-1}) – doubly degenerate in-plane bending vibration.

So far as the planar CO_3^{2-} group is not affected by the force field, it possesses the point symmetry D_{3h} . The ν_1 fundamental is only Raman-active, ν_2 is IR-active, and

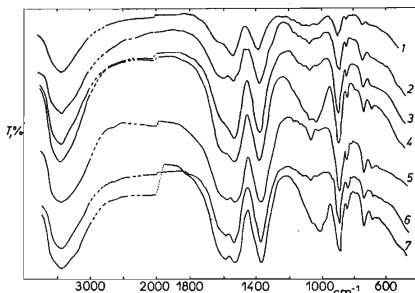


FIG. 1

Infrared Absorption Spectra of Liebigit in Potassium Bromide Disks

1 M 38, 2 M 45, 3 M 27, 4 M 47, 5 M 31, 6 M 32, 7 M 43.

ν_3 and ν_4 are both IR- and Raman-active. Thus only three bands of the fundamentals are observable in the IR spectrum^{11,12}. The number of the bands increases if the carbonate ion is embedded in a crystal lattice site of lower symmetry or if bonding forces between the carbonate oxygen atoms and other atoms in the crystal operate. If the resultant space symmetry group becomes isomorphous with some of the point groups C_{2v} , C_s , or C_1 , the degeneracy of the vibrational modes ν_3 and ν_4 is removed and all vibrations are then both IR- and Raman active. The number of the IR bands rises thus to the total of six. If in addition several crystallographically nonequivalent carbonate groups are present in the elementary cell, the number of the active frequencies is accordingly multiplied. The CO_3^{2-} ion behaves as a monodentate (symmetry C_s or C_{2v}) or a bidentate (symmetry C_{2v}) ligand¹³⁻¹⁵. A discrimination based on the IR spectra is rather difficult. According to some authors¹⁶, it is possible to make use of the splitting of the ν_3 fundamental, which for a monodentately bonded carbonate group amounts to about 100 cm^{-1} , for a bidentately bonded group amounts to about 300 cm^{-1} . Ross¹⁷ states that in the former case the splitting does not exceed 150 cm^{-1} and in the latter case is not lower than 300 cm^{-1} , the highest wavenumber values for the antisymmetric stretching fundamental lying in the ranges $1500-1450\text{ cm}^{-1}$ and $1640-1590\text{ cm}^{-1}$ for the two types of the carbonate ligand, respectively. According to the authors^{18,19}, this criterion is not sufficient. The position of the $\nu_2(\text{CO}_3^{2-})$ band has been employed for discriminating between the structural types, too²⁰. We have not found this parameter useful for the establishing of the structural type, since the frequency of the ν_2 mode is affected by several factors, such as the cation charge and size, for instance.

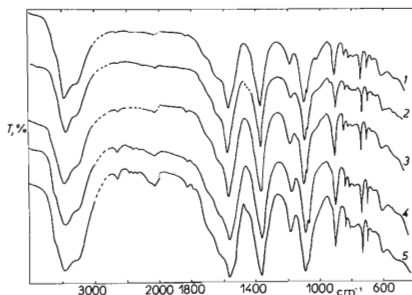


FIG. 2

Infrared Absorption Spectra of Schroeckingerite in Potassium Bromide Disks
1 M 50, 2 M 54, 3 M 52, 4 M 51, 5 M 65.

The presence of water is manifested in the spectrum by the symmetric $\nu_1(\text{H}_2\text{O})$ and antisymmetric $\nu_3(\text{H}_2\text{O})$ stretching vibration bands in the range $3550\text{--}3200\text{ cm}^{-1}$ and by the band of the bending vibration $\nu_2(\text{H}_2\text{O})$ at $1630\text{--}1600\text{ cm}^{-1}$. The weak bands in the region $600\text{--}300\text{ cm}^{-1}$ are due to librations of the water molecules^{14,21,22}. The OH^- ions are characterized by the $\nu(\text{OH}^-)$ stretching vibration at 3700 to 3500 cm^{-1} and the $\text{M}\text{--}\text{O}\text{--}\text{H}$ vibration in the range $1200\text{--}600\text{ cm}^{-1}$ (see^{14,17,23}). In some cases oxonium ions, H_3O^+ , can be present, giving rise to four vibrational bands^{22,24}.

The IR spectra of liebigite, voglite, schroeckingerite, and andersonite as measured by us are shown in Figs 1–4, their elucidation is given in Tables II–VI.

The $\nu_3(\text{UO}_2^{2+})$ stretching vibration in complex dioxo-tricarbonatouranates (VI) appears in the region $917\text{--}877\text{ cm}^{-1}$. NH_4^+ , K^+ , Rb^+ , and Cs^+ salts exhibit this vibration at $883\text{--}877\text{ cm}^{-1}$, introduction of alkali earth metals and water in the molecule brings about an increase of the wavenumber of this vibration. Liebigite,

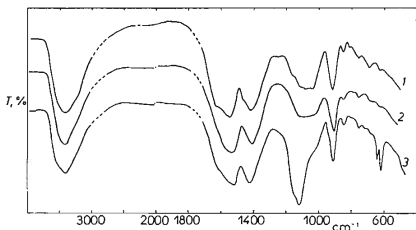


FIG. 3

Infrared Absorption Spectra of Voglite in Potassium Bromide Disks

1 M 17, 2 M 19, 3 M 20.

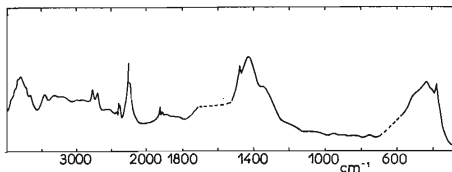


FIG. 4

Infrared Absorption Spectrum of Synthetic Andersonite in Potassium Bromide Disk

y-axis: % T.

TABLE II

Interpretation of the Infrared Spectrum of Liebigite

Characterization of the bands: intensity: VS very strong, S strong, MS medium strong, M medium, MW medium weak, W weak, VW very weak; band shape: s sharp, b broad, sh shoulder; wavenumbers in parentheses can be read off with an accuracy poorer than 0.5%, wavenumbers in square brackets indicate peaks which need not be due to the substance investigated; several in braces indicate a considerable overlap of the bands.

Band No	Wavenumbers ^a cm ⁻¹	Intensity, shape	Assignment
1	682 < 678 690	W	$\nu_4^{E'}(\delta)\text{CO}_3^{2-}$
2	737 < 733 740	MW, s	$\nu_4^{E'}(\delta)\text{CO}_3^{2-}$
3	841 < 838 843	W, s	$\nu_2^{A'}(\gamma)\text{CO}_3^{2-}$
4	890 < 882 893	S	$\nu_3(\text{UO}_2^{2+})$
5	(902) < 900 903	sh	$\nu_3(\text{UO}_2^{2+})$
6	(932) < 927 935	sh	$\nu_3(\text{UO}_2^{2+})$
7	1 020 < 1 010 1 028	VW-M	$\nu_1^{A'}(\nu_s)\text{CO}_3^{2-}$? δOH ? νSiO ?
8	1 069 < 1 068 1 071	WM	δOH ? νSiO ?
9	1 110 < 1 108 1 115	VW ?	δOH ? νSiO ?
10	1 378 < 1 375 1 383	VS	$\nu_3^{E'}(\nu_{as})\text{CO}_3^{2-}$
11	1 538 < 1 535 (1 520) 1 540	S	$\nu_3^{E'}(\nu_{as})\text{CO}_3^{2-}$
12	(1 590) < 1 589 (1 573) 1 595 (variable)	S-W, sh-s	$\nu_2(\text{H}_2\text{O})$?
13	(1 632) < 1 630 1 635	W, sh	$\nu_2(\text{H}_2\text{O})$
14	3 450 < 3 430 3 460	S, sh ^b	νOH

^a Left: the most likely value for the pure substance; right: the lowest and the highest values within the assembly tested (8 samples); ^b shoulders from the left and from the right.

TABLE III

Interpretation of the Infrared Spectrum of Schroeckingerite Characterization of the Bands as in Table II.

Band No	Wavenumbers ^a cm ⁻¹	Intensity, shape	Assignment	Huang, Kerr (ref. 6) ^b
1	(525) < 520 533	VW, b		
2	608 < 603 609	WM	$\nu_4^F(\text{SO}_4^{2-})$	
3	(665) < 663 668	VW		
4	705 < 701 706	MW, s	$\nu_4^E(\text{CO}_3^{2-})$	
5	739 < 735 741	M, s	$\nu_4^E(\text{CO}_3^{2-})$	738 W (-1)
6	(750)	sh		
7	790 < 789 797	VW, b		
8	816 < 814 818	W, s	$\nu_2^A(\text{CO}_3^{2-})$	
9	842 < 839 843	WM, s	$\nu_1(\text{UO}_2^{2+})?$	844 W (+2)
10	903 < 900 905	MS, s	$\nu_3(\text{UO}_2^{2+})$	913 M (+10)
11	932 < 930 936	VW	$\nu_1^A(\text{SO}_4^{2-})?$	
12	1 015 < 1 014 1 017	VW	$\nu_1^A(\text{SO}_4^{2-})?$	
13	1 078 < 1 075 1 080	W, s	$\nu_1^A(\text{CO}_3^{2-})$	
14	1 093 < 1 092 1 094	S, s	$\nu_3^E(\text{SO}_4^{2-})$	1 098 M (+5)
15	1 182 < 1 179 1 184	MW	$\nu_3^E(\text{SO}_4^{2-})$	1 160 W (-22)
16	1 367 < 1 364 1 369	VS	$\nu_3^E(\text{CO}_3^{2-})$	1 390 S (+23)
17	1 572 < 1 570 1 574	VS	$\nu_3^E(\text{CO}_3^{2-})$	1 558 S (-14)
18	(1 638) < 1 635 1 640	WM, sh	$\nu_2(\text{H}_2\text{O})$	
19	2 640 < 2 633 2 645	W		

TABLE III
(Continued)

Band No	Wavenumbers ^a cm ⁻¹	Intensity, shape	Assignment	Huang, Kerr (ref. ⁶) ^b
20	(3 260) < 3 250 3 270	M, sh	νOH	
21	3 455 < 3 450 3 460	S	νOH	3 510 M (+55)
22	(3 620) < 3 590 3 630	sh	νOH	

^a Left: the most likely value for the pure substance; right: the lowest and the highest values within the assembly tested (6 samples); ^b differences between the wavenumbers found by us and those reported by Huang and Kerr⁶ are given in parentheses.

Ca₂[UO₂(CO₃)₃].(8–11) H₂O, shows it at 893–882 cm⁻¹ (our measurements), K₂Ca₃[UO₂(CO₃)₃]₂.10 H₂O at 893 cm⁻¹ (ref.²⁵), synthetic and natural andersonite, Na₂Ca[UO₂(CO₃)₃].6 H₂O, at 901–899 cm⁻¹, schroeckingerite, NaCa₃[UO₂.(CO₃)₃]SO₄F.10 H₂O, at 905–900 cm⁻¹ (our measurements), 908 cm⁻¹ (ref.²⁵), 913 cm⁻¹ (ref.⁶), and finally voglite, described by the hitherto not verified formula Ca₂Cu[UO₂(CO₃)₄].6 H₂O (ref.³), at 903–902 cm⁻¹ (our measurements). The uranyl group forms coordination polyhedra – in complex dioxo-tricarbonatouranates(VI) hexagonal bipyramids, with the two oxygen atoms (U—O) in the apexes and six oxygen atoms (U—O_{II}) belonging to the carbonate groups in the uranyl equatorial plane. The U—O_I bond lengths are only slightly affected by the number of anions in the equatorial coordination²⁵.

The spectra indicate that the symmetry of the CO₃²⁻ ion is reduced from D_{3h} to C_{2v} or lower. The X-ray diffraction analysis has evidenced that the dioxo-tricarbonatouranate(VI) anion [UO₂(CO₃)₃]⁴⁻ and the [NpO₂(CO₃)₃]⁴⁻ anion are isostructural, as found for the potassium salts by Germanov-Gorbenko and Krylov³¹, and contain three bidentately bonded CO₃²⁻ groups in the equatorial plane of the uranyl or neptunyl groups^{26–30}. This has been confirmed also for the calcium and sodiumtripotassium salts based on the analysis of the spectra^{32,33} in the region 30000–20000 cm⁻¹. This can be correlated with the splitting of the doubly degenerate ν₃(CO₃²⁻) stretching vibration, which – for some dioxo-tricarbonatouranates(VI) as measured by other authors and for liebigite, andersonite, voglite, and schroeckingerite measured by us (Table VI; refs^{6,34–40}) – falls within the range 233–158 cm⁻¹, the ν_{3a}(CO₃²⁻) and ν_{3b}(CO₃²⁻) vibrational wavenumbers lying in the regions 1402–1329 and 1597 to

1500 cm^{-1} , respectively. From the X-ray diffraction data on synthetic dioxo-tricarbonatouranates(VI) it is known that in those substances the carbonate groups are bonded as a bidentate ligand. The similarity of the IR characteristics pertaining to the carbonate group vibrations in these compounds and in the mineral phases justifies the conclusion that in the structure of the minerals, the same coordination occurs in the uranyl equatorial plane, despite the fact that the criteria given in the book by Ross¹⁷ are not satisfied.

The $\nu_{4a}(\text{CO}_3^{2-})$ and $\nu_{4b}(\text{CO}_3^{2-})$ vibrations of the minerals examined by us, which in fact are crystallohydrates, lie in the range 705–678 and 745–725 cm^{-1} , respecti-

TABLE IV
Interpretation of the Infrared Spectrum of Voglite
Characterization of the bands as in Table II.

Band No	Wavenumbers, cm^{-1} , intensity, shape				Assignment	
	M 17	M 18	M 19	M 20		
1	(535) sh	(525) bsh				
2	610 W	615 VWb	(615) Wb	612 MWs ^a 633 Ws ^a	$\nu_4(\text{CO}_3^{2-})$ ^a $\nu_4(\text{SO}_4^{2-})$	
3		685 W	(675) Wb			
4	741 W	745 VWsh	742 W	741 W	$\nu_4(\text{CO}_3^{2-})$	
5		778 W				
6	796 VW	794 W	(795) VW			
7	841 W	(843) VWb	836 W	833 W	$\nu_2(\text{CO}_3^{2-})$	
8	875 sh 903 MS	903 M	903 MS	902 MS	$\nu_3(\text{UO}_2^{2+})$	
9	1 030	(1 005) Wsh	1 015	(1 020) sh		
10	(1 053)	1 032 Wsh	} M		$\nu_1(\text{CO}_3^{2-})$	
11	(1 073) MS	1 073 S		...		
12	(1 105)			1 110	1 115 VS ^a	^a $\nu_3(\text{SO}_4^{2-})$
13	1 151 Wb	(1 160) sh		(1 170) sh	$\delta(\text{OH})?$	
14	1 410 S (1 465) Wsh	1 402 MS	1 410 S	1 420 S	$\nu_3(\text{CO}_3^{2-})$	
15	1 540 VS	1 560 S	(1 535) VSsh (1 560) sh	1 512 S (1 560) sh	$\nu_3(\text{CO}_3^{2-})$	
16	1 618 Wsh	(1 618) Wsh	(1 620) sh	(1 620) sh	$\nu_2(\text{H}_2\text{O})$	
17	(3 340) Msh				} νOH	
18	3 385 VS	3 440 VS	3 400 S	3 400 S		
19	[3 557] Ws		(3 550) Wsh	(3 550) sh		

^a Probably due to the presence of the sulfate ion.

vely; these values as well as the value of the splitting are higher than as found for anhydrous alkali dioxo-tricarbonatouranates(VI) (694–684 and 722–714 cm^{-1} , respectively). The $\nu_2(\text{CO}_3^{2-})$ and $\nu_1(\text{CO}_3^{2-})$ vibrations lie at higher wavenumbers (ν_2 843–838 cm^{-1} and 852–839 cm^{-1} , ν_1 1030–1010 cm^{-1} and 1049–1038 cm^{-1}).

TABLE V

Interpretation of the Infrared Spectrum of Synthetic Andersonite
Characterization of the bands as in Table II.

Band No	Wavenumbers, cm^{-1} intensity, shape	Assignment	Natural andersonite ⁶
	(235) sh	—	—
1	254 VW	—	—
	269 W, s	—	—
3	284 M	—	—
	(317) sh	—	—
4	344 W	—	—
5	424 W	—	—
6	475 VW, vb	—	—
	(530) VW, vb	—	—
8	613 VW	—	—
9	698 W	$\nu_4(\text{CO}_3^{2-})$	697 W
10	725 W, s	$\nu_4(\text{CO}_3^{2-})$	727 W
11	(785) W, b	—	—
12	832 VW, s	$\nu_2(^{13}\text{CO}_3^{2-})$	—
13	844 W, s	$\nu_2(\text{CO}_3^{2-})$	848 W
	[851] VW, ssh	—	—
14	899 MS, s	$\nu_3(\text{UO}_2^{2+})$	901 S
	(912)	$\nu_3(\text{UO}_2^{2+})$	913 sh
15	1 080 W, s	$\nu_1(^{13}\text{CO}_3^{2-})$	1 020 W, b
			1 080 W, b
16	1 091 VW, s	—	—
17	not measured — Nujol	$\nu_3(\text{CO}_3^{2-})$	1 385 VS
18	1 521 W, s	$\nu_3(\text{CO}_3^{2-})$	1 535 sh
	1 570 S	$\nu_3(\text{CO}_3^{2-})$	1 580 VS
20	(1 660) W, b	$\nu_2(\text{H}_2\text{O})$	(1 660) inflexion
	[2 110] VW, b	—	—
21	2 605 VW	—	—
22	(3 200) W, sh	νOH	—
	3 405 MS	νOH	3 510 S, b
24	(3 500) sh	νOH	—
25	3 645 MW, s	νOH	—

With rutherfordine, $\text{UO}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$, the splitting of the $\nu_4(\text{CO}_3^{2-})$ mode is exceedingly low (704–701 and 782–781 cm^{-1}), the $\nu_2(\text{CO}_3^{2-})$ vibrational wavenumber is considerably lower (806–804 cm^{-1}), and the ν_1 mode appears at very high wavenumbers (1112–1105 cm^{-1}). Sharpite displays more bands, which is due to the presence of nonequivalent carbonate groups^{3,5}.

While the alkali dioxo-tricarbonatouranates(VI) are anhydrous, the minerals under examination contain a relatively great number of crystal water molecules. The presence of molecular water is manifested in the spectra by the $\nu_2(\text{H}_2\text{O})$ bending vibra-

TABLE VI

Comparison of the Positions of the $\nu_3(\text{UO}_2^{2+})$ and $\nu_3(\text{CO}_3^{2-})$ Bands and of the Splitting of the $\nu_3(\text{CO}_3^{2-})$ Mode for Natural and Synthetic Dioxo-Tricarbonatouranates(VI) (cm^{-1})

Substance	$\nu_3(\text{UO}_2^{2+})$	$\nu_{3a}(\text{CO}_3^{2-})$	$\nu_{3b}(\text{CO}_3^{2-})$	Δ_a	Ref.
Rutherfordine	982	1 420	1 507	87	34, 35
Rutherfordine	985	~1 430	~1 525	~95	36
UO_2CO_3 hydrotherm. \varnothing	978	1 424	1 522	98	37
$\text{UO}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$ norm. conditions	954	1 427	1 543	116	38
Sharpite \varnothing	935.5	1 418	1 540	122	34, 45
$(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$	883	1 332	1 500	168	39
$\text{K}_4[\text{UO}_2(\text{CO}_3)_3]$	881/882	1342/ 1364	1539/ 1597	209/233	40/39
$\text{Rb}_4[\text{UO}_2(\text{CO}_3)_3]$	877	1 338	1 570	232	40
$\text{Cs}_4[\text{UO}_2(\text{CO}_3)_3]$	877	1 357	1 551	194	40
Andersonite	901	1 385	(1 535) 1 580 1 580	(150) 195	6
Andersonite synth.	899	not measured	1 570	—	this work
Andersonite synth.	917	~1 385	(~1 525) ~1 575	(~140) ~190	36
Liebigite \varnothing	888	1 378	1 538 (1 590)	160 (212)	this work
Voglite	903	1 402	1 560	158	this work
Schroekingierite	913	1 390	1 558	168	6
Schroekingierite \varnothing	903	1 364	1 572	208	this work
Schroekingierite synth.	908	—	—	—	25
$\text{K}_2\text{Ca}_3[\text{UO}_2(\text{CO}_3)_3]_2 \cdot 10 \text{H}_2\text{O}$	893	—	—	—	25
$\text{K}_4[\text{NpO}_2(\text{CO}_3)_3]$	873	1 309	1 538	229	31

^a $\nu_{3a}(\text{CO}_3^{2-}) - \nu_{3b}(\text{CO}_3^{2-})$.

tions, found at $1635-1630\text{ cm}^{-1}$ for liebigite, 1660 cm^{-1} for andersonite, 1640 to 1635 cm^{-1} for schroeckingerite, and $1645-1618\text{ cm}^{-1}$ for voglite, and by the stretching vibrations, appearing at $3460-3430$ and $3580-3560\text{ cm}^{-1}$ for liebigite, 3405 and 3645 cm^{-1} for andersonite (Huang and Kerr⁶ 3510 cm^{-1}), $3270-3250$ and $3630-3590\text{ cm}^{-1}$ for schroeckingerite, and $3440-3385$ and $3560-3550\text{ cm}^{-1}$ for voglite. The presence of OH^- or H_3O^+ ions cannot be inferred from the IR spectra unless *e.g.* partially deuterated substances are studied.

In the spectrum of schroeckingerite, the vibrational bands at $1094-1093$ and $1184-1179\text{ cm}^{-1}$ belong to the $\nu_3(\text{SO}_4^{2-})$ mode, those at $609-603$ and 668 to 663 cm^{-1} to the $\nu_4(\text{SO}_4^{2-})$ mode, and that at $1017-1014\text{ cm}^{-1}$ to the $\nu_1(\text{SO}_4^{2-})$ mode. The only slight variations within a larger group of the measured spectra of liebigite and schroeckingerite indicate in both cases the existence of well defined stable structures, the differences in the various spectra of voglite (whose composition and structure are not known and which has not yet been synthesized), on the other hand, give evidence of a great variability of the bonding of water and possibly also of the cation sphere in the structure. The spectra of schroeckingerite obtained by us resemble the published spectrum⁶ (some bands in the latter overlap or do not appear and some of them are more or less shifted).

From the analysis of all the known data on the structure and composition in conjunction with the elucidation of the IR spectra, the following conclusions can be drawn: In liebigite and andersonite, uranium possesses the coordination number eight, the uranyl group six, the latter forming the above mentioned coordination polyhedron — hexagonal bipyramid with the two oxygen atoms in the apexes and with six oxygen atoms of three bidentately bonded carbonate ligands in the equatorial plane of the uranyl. The low wavenumber of the $\nu_3(\text{UO}_2^{2+})$ mode indicates the insular character of the structure, where each carbonate anion belongs to one uranyl group only, forming thus the tricarbonato complex; so it affects appreciably the equatorial uranyl field, which results in a loosening of the $\text{U}-\text{O}_1$ uranyl bond. These anion islands are likely to form layers mutually bonded by the electrostatic forces of the cation and by hydrogen bonds. More complicated is the situation with schroeckingerite, if the anion $[\text{UO}_2(\text{CO}_3)_3]\text{SO}_4\text{F}^{7-}$ is assumed, and with voglite, if the original analysis is assumed to be correct and hence the anion $[\text{UO}_2(\text{CO}_3)_4]^{6-}$ to occur. Inasmuch as the dioxo-tricarbonatouranate(VI) anion is considerably more stable than the dioxo-trisulfatouranate(VI) anion, hence the bonding of the carbonate ligands in the uranyl equatorial plane is stronger than that of the sulfate ligands⁴¹, the existence of the complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ in schroeckingerite can be taken for proved as well. The SO_4^{2-} or F^- ions are not coordinated in the inner coordination sphere and the problem of their coordination remains open. Povarennykh⁴² regards a considerably more complex structure of the uranyl-anion layers in schroeckingerite. In voglite it is necessary to consider also the possibility of occurrence of the complex $[\text{UO}_2 \cdot (\text{CO}_3)_4]^{6-}$ analogous to the known anion $[\text{UO}_2(\text{NO}_3)_4]^{2-}$ in which two NO_3

groups are bonded bidentately and two monodentately⁴³. It is, however, equally possible that in this case, too, the relatively very stable complex dioxo-tricarbonatouranate(VI) anion is present. So long as the single, more than 120 years old and rather questionable analysis cannot be proved or disproved, this question remains open too. The stepwise dehydration of andersonite, liebigite, and schroeckigerite during their thermal decomposition evidence that in these substances the various water molecules are coordinationally bonded by forces of different strengths⁴⁴⁻⁴⁶.

The authors wish to thank Mrs L. Šourková, Institute of Nuclear Research, Řež, for technical assistance during the IR spectral measurements, and to Mrs E. Kaprálová, Research Chemical Laboratory, National Museum, Prague, for the X-ray diffractograms of the minerals studied.

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Translated by P. Adámek.